

X-Ray Absorption Fine Structure at the Cesium L_3 Absorption Edge for Cesium Sorbed in Clay Minerals

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1 Introduction

The Contamination of soil with radioactive materials released in the Fukushima Daiichi Nuclear Power Plant accident caused by the Great East Japan Earthquake on March 11, 2011 is still a significant problem. Contamination of radioactive materials also occurred from the Chernobyl Nuclear Power Plant accident in 1989. Research results from after these accidents revealed that radioactive cesium released into the atmosphere diffused into the soil over time. Reports showed that radioactive cesium in soil is fixed in particular clay minerals[1],[2].

In this research, we employed Cs L_3 edge NEXAFS to determine the local electronic structures of Cs sorbed in two types of clay minerals: vermiculite and kaolinite. These two types of clay minerals were chosen because they have different structures and Cs-fixing ability. Vermiculite is a 2:1 phyllosilicate structure, with 2 tetrahedral silica sheets for every one octahedral alumina sheet and a high Cs-fixing ability. Kaolinite has a 1:1 type structure with a low Cs-fixing ability[1]. Furthermore, vermiculite have both internal and external site on the other hand, kaolinite has external surface only. We succeeded in measuring Cs L_3 -edge NEXAFS spectra of these clay minerals using the fluoresce-XAFS system[3] that was recently developed. As a demonstration of this method, we present NEXAFS spectral changes that are dependent on the clay minerals and water environment.

2 Experiment

The vermiculite samples were produced in Ono-machi, Fukushima Prefecture, Japan. The sample had a particle size of 2 μm or less and was a mixed crystal of weathered biotite that adsorbs Cs well. The detailed structure of this sample was reported by Motokawa *et al.*[4]. Kaolinite was purchased from Geo-Science Materials Nichika Co., Ltd. (Kyoto, Japan). Reagent-grade CsCl was purchased from Wako Pure Chemical Industries, Co., Ltd. (Osaka, Japan) and used without further purification. The water used in this study was deionized with a Milli-Q purification system (Merck Millipore, Billerica, MA).

All experiments were conducted at BL-27A of the soft X-ray synchrotron radiation beam line of Photon Factory, KEK. In recent years, we have developed a fluorescence XAFS measurement system on this beam line[3]. NEXAFS was measured by fluorescence yield. A silicon drift detector (SDD) (Amptek Co., Ltd, United States of America. FAST SDD) was used as a detector for the fluorescent X-rays.

3 Results and Discussion

We present the use of near-edge X-ray absorption fine structure (NEXAFS) to investigate local electronic structures of cesium ions sorbed in two types of clay minerals (vermiculite and kaolinite) with a different capacity to fix Cs. NEXAFS is element specific because X-ray absorption edges of different elements have different energies. However, the energy of the Cs L_3 absorption edge is close to that of the K-edge of titanium generally contained in clay minerals. Therefore, Cs L_3 -edge NEXAFS measurements of Cs in clay minerals have not yet succeeded. In this study, we confirmed the peak intensity between vermiculite and kaolinite in the Cs L_3 -edge NEXAFS spectra by separately monitoring T $K\alpha$ and Cs $L\alpha$ fluorescence X-rays. To clarify the identification of NEXAFS spectra, theoretical calculations were performed using the discrete variational $X\alpha$ molecular orbital method (DV- $X\alpha$), and peak identification was achieved. The difference in peak intensity was explained by the difference in the electron density of unoccupied molecular orbitals. We studied the influence of water molecules and found a change in the electron densities of unoccupied molecular orbitals caused by the coordination of water molecules.

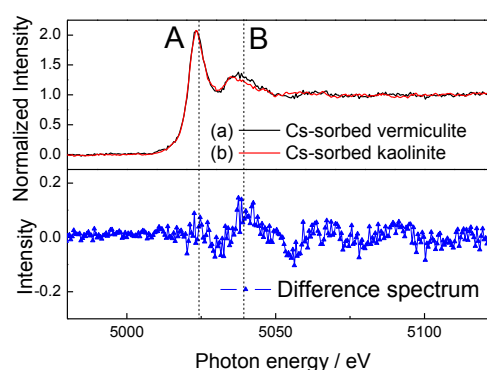


Fig. 1: Comparison of Cs L_3 -edge NEXAFS spectra for Cs-sorbed vermiculite (black line) and Cs-sorbed vermiculite in water (red line) and difference spectra (blue line).

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